

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference B01/0960PC	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP2002/014786	International filing date (day/month/year) 27 December 2002 (27.12.2002)	Priority date (day/month/year) 27 December 2001 (27.12.2001)
International Patent Classification (IPC) or national classification and IPC C23C 22/05, 18/31, 18/48, 22/06, C25D 11/08, C09D 125/08, C25D 3/56, C08G 8/10		
Applicant BASF AKTIENGESELLSCHAFT		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 11 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 17 July 2003 (17.07.2003)	Date of completion of this report 25 March 2004 (25.03.2004)
Name and mailing address of the IPEA/EP	Authorized officer
Facsimile No.	Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/EP2002/014786

I. Basis of the report

1. With regard to the elements of the international application:*

 the international application as originally filed the description:

pages 1-33, as originally filed

pages _____, filed with the demand

pages _____, filed with the letter of _____

 the claims:

pages _____, as originally filed

pages _____, as amended (together with any statement under Article 19

pages _____, filed with the demand

pages 1-12, filed with the letter of 12 March 2004 (12.03.2004)

 the drawings:

pages _____, as originally filed

pages _____, filed with the demand

pages _____, filed with the letter of _____

 the sequence listing part of the description:

pages _____, as originally filed

pages _____, filed with the demand

pages _____, filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

 the language of a translation furnished for the purposes of international search (under Rule 23.1(b)). the language of publication of the international application (under Rule 48.3(b)). the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

 contained in the international application in written form. filed together with the international application in computer readable form. furnished subsequently to this Authority in written form. furnished subsequently to this Authority in computer readable form. The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished. The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. The amendments have resulted in the cancellation of: the description, pages _____ the claims, Nos. _____ the drawings, sheets/fig _____5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rule 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

- restricted the claims.
- paid additional fees.
- paid additional fees under protest.
- neither restricted nor paid additional fees.

2. This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- complied with.
- not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- all parts.
- the parts relating to claims Nos. _____

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/EP/14786

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	YES
	Claims	1-12
Inventive step (IS)	Claims	YES
	Claims	1-12
Industrial applicability (IA)	Claims	YES
	Claims	NO

2. Citations and explanations

1. This report makes reference to the following search report citations; the same numbering will be used throughout the procedure:

D1: WO 01 48264 A (HONDA TAKUMI; SAKO RYOSUKE (JP); UENO KEICHI (JP); HENKEL CORP (U)) 5 July 2001 (2001-07-05)

D2: DE 196 21 184 A (HENKEL KGAA) 4 December 1997 (1997-12-04)

D3: DE 100 10 758 A (HENKEL KGAA) 6 September 2001 (2001-09-06), cited in the application

D4: US-A-4 978 399 (KODAMA KENJI ET AL) 18 December 1990 (1990-12-18)

D5: US-A-5 494 535 (KELLER HARALD ET AL) 27 February 1996 (1996-02-27)

D6: DE 31 21 015 A (BLASBERG GMBH & CO KG FRIEDR) 16 December 1982 (1982-12-16)

D7: EP-A-0 250 867 (IBM) 7 January 1988 (1988-01-07)

D8: US-A-4 199 417 (BORRUSO MARIANO) 22 April 1980 (1980-04-22)

D9: EP-A-0 649 918 (ROHCO INC MCGEAN) 26 April 1995 (1995-04-26)

D10: US-A-3 386 898 (RUSHMORE JOHN D) 4 June 1968 (1968-06-04)

D11: US-A-5 478 463 (BROWNAWELL DARRELL W ET AL)

26 December 1995 (1995-12-26)

D12: US-A-5 134 176 (SHU PAUL) 28 July 1992
(1992-07-28)

D13: EP-A-0 736 770 (ANDA BIOLOG SA) 9 October 1996
(1996-10-09)

D14: US-A-5 705 537 (HARTMAN JR JOHN J ET AL)
6 January 1998 (1998-01-06)

D15: US-A-4 181 787 (ENGLIN BORIS ET AL)
1 January 1980 (1980-01-01)

2. Prior art and novelty

2.1 D2 discloses a method and a solution for phosphating metal surfaces which, in addition to Zn, Mn and phosphate ions, contains one or a plurality of polymers which are preferably amino-group-containing poly(vinylphenol) derivatives. As examples of these polymers, a), b) and c) are set out with structural formulae on pages 6, 7 and 8. At least one of the Y substituents on the benzene ring has to be an amine or ammonium group. Thus these examples, a), b) and c), in each case represent an amino-group-containing polymer or an ammonium-group-containing polymer, and in the case in which W = H, also a polymer containing phenolic units. In example d), however, one or a plurality of the polymers a), b) and c) is/are reacted with a phenolic component (phenols, tannins, novolac resins or lignin compounds) in the presence of an aldehyde or ketone to produce a condensation polymer. Therefore this polymer is composed of an amino-group-containing or ammonium-group-containing polymer and phenolic units.

Examples 3 to 6 of the table on page 11 and on page 8, line 56, to page 9, line 39, show Mannich reaction products consisting of polyvinylphenol, paraformaldehyde

and glucamine or other polyamines. The aminomethyl-substituted polyamine on page 9 should be mentioned in particular here, since it differs from the polyvinylamine used in the application only by the additional methylene group. In addition, the phosphating solution contains further components, such as mineral acids, and additives, such as accelerators, for example (page 3, lines 36 to 54). Method steps, such as degreasing and scouring, are included in the embodiment on page 10.

Claims 1 to 12 are not considered novel over D2 since the independent claims of the present application do not describe the reaction of the conversion of compounds aa), ab) and optionally ac) in further detail and it is conceivable to use a reaction in which a polyvinylamine, a phenol and a formaldehyde are reacted (optionally using further reactants) such that the Mannich reaction product which is mentioned in D2, page 9, and consists of polyvinylphenol, paraformaldehyde and the aminomethyl-substituted polyamine is produced.

2.2 The disclosure in D3, cited by the applicant, also resembles D2 to a large extent.

2.3 D8 discloses compositions for galvanising baths. Column 3, lines 21 to 25, states that a reaction product consisting of polyethyleneimine and vanillan can be added to the bath solution in example 5. These starting substances clearly react in the sense of the Michael reaction set out on page 12 of the present application, since vanillan, like benzoquinone, has a keto group with a double bond in the α position.

The bath solution also contains other components, such that, even though parts of claims 2 to 5 are vague, these claims cannot be considered novel.

Since D8 further indicates that the solutions are used for electrochemical deposition on metal substrates (column 1, lines 5 to 9), claims 6 to 11 also lack novelty over D8.

2.4 D6 concerns a method of activating pickled surfaces. According to claims 1 to 10, a solution is used which *inter alia* preferably contains a polyethyleneimine and a phenol (claim 6). It is to be assumed that the polyethyleneimine and phenol react at least partially with each other. The solution also contains transition metal ions, such that claims 1, 2 and 12 lack novelty.

2.5 Example 16 of D15 (column 10) describes the reaction of polyethyleneimine with hydroquinone in the presence of concentrated HCl. The resulting material can be dissolved in various solvents. Similar reactions are indicated in examples 35 and 40 (columns 13 and 14).

The reaction mixture present when the water and HCl have not been fully distilled off is prejudicial to the novelty of claims 1, 2 and 12.

2.6 In D11, different polymers are formed by reacting polyamines, for example, polyethyleneamine and polyethyleneimine, with phenol-formaldehyde compounds or benzoquinone (polymers C, G, H, L, M, N and example 4, columns 13 to 17). The reaction is carried out in methanol, for example. Claims 1 and 12 are thus not novel over D11.

2.7 D12 discloses a mixture of water and a reaction product consisting of a polyvinylamine copolymer, an aldehyde and a phenol (abstract, and column 4, line 22, to column 5, line 28). Claims 1 and 12 are thus not novel over D12

2.8 D13 (page 7, lines 1 to 3) describes the reaction of polylysine with a hapten in the presence of benzoquinone. It is implicit that this reaction occurs in a solvent. Therefore claims 1 and 12 are not novel over D13.

2.9 D1 describes a composition and a method of treating metal surfaces. The composition contains a dissolved or undissolved organic resin, a dissolved vanadium compound and a dissolved compound which contains at least one of the metals Zr, Ti, Mo, W, Mn or Ce, as well as water (abstract, and page 3, line 26, to page 8, line 4). Table 1 describes the resins a3, a6 and a8, which contain five or ten hydroxyphenyl-CH₂-NH-CH₂ repeat units and a terminal phenolic group. They are applied as an aqueous formulation to metal surfaces. Page 9, lines 15 to 18, states that the resins can be produced from phenolic or bisphenolic compounds by condensation with formaldehyde.

D1 also indicates that the treatment mixture can contain further components, such as mineral acids (page 7, lines 28 to 35), dispersants and emulsifying agents (page 11, line 25, to page 13, line 3). The possible vanadium compounds are listed on page 9, lines 19 to 31. Other organic compounds are described on page 11, lines 8 to 24. Page 19 describes the use of the treatment mixtures, which include *inter alia* steps in which the metal substrate is degreased and washing steps.

Claims 1 to 12 are considered novel over D1 since it is not assumed that the compounds aa), ab) and optionally ac) can be reacted one with another such that a polymer disclosed in D1 is obtained.

2.10 Documents D1 to D3 show that the elements that appear in the dependent claims (with the exception of claim 12) belong to the prior art in the field of the treatment of metal surfaces.

2.11 The other search report citations are not considered prejudicial to novelty.

2.12 Since claims 1 to 12 of the present application are not considered novel, in particular with respect to D2 and D8, the question arises as to whether components A in examples A1 to A9 of the present application can be considered novel.

Component A5 is already described in D11 (e.g. polymers L and M). The other components, A1 to A4, and A6 to A9, are considered novel since none of the prior art documents describes the reaction of a polyamine with catechol. Therefore a claim 1 directed to the reaction product of polyvinylamine, polylysine, polyvinylimine or poly(vinylamine-co-vinylformimide) with catechol in the presence of formaldehyde would be considered novel.

If such a claim indicated that formaldehyde were merely optional, it would go beyond the original disclosure. Moreover, formaldehyde is considered an essential technical element for arriving at components A1 to A4 and A6 to A9 by reacting catechol with one of the above-mentioned polyamines.

3. Inventive step

3.1 Only documents D1 to D5 and D8 concern metal-treatment solutions.

D1 to D4 already disclose polymers that contain phenolic units and amino groups and are produced by reacting *inter alia* ketones or aldehydes in the presence of an amine, in a Mannich reaction. However, it is noted that the polymers used in D1 to D4 do not contain any polyethyleneimine or polyvinylamine structural units. In addition, the polymers in D1 to D4 are composed of polyphenol units.

D5 (column 1, lines 17 to 20, and column 1, line 65, to column 2, line 48) discloses treatment solutions containing the hydrolysis product of a polyvinylamide, for example, polyvinylamine. D8 mentions the reaction product of polyethyleneimine and vanillan as brightening agent in nickel electroplating.

3.2 The technical problem addressed is now regarded as that of proposing alternative polymers to D1 to D4 for compositions for treating metal surfaces. To that end, proceeding from those documents, a person skilled in the art would vary both the phenolic component and the amine component. In this context, it is obvious to use amines which are already used as a component in such solutions, that is, polyethyleneimine or polyvinylamine, for example (D5, D8).

However, this procedure would produce compositions composed of polyvinylphenol and polyvinylamine or polyethyleneimine, whereas, in the abovementioned examples, the polymer contains individual catechol units.

3.3 Thus it does not appear possible to derive components A1 to A4 and A6 to A9 from the prior art.

4. Claims 1 to 12 meet the industrial applicability requirement (PCT Article 33(4)) since the technical subject matter of the present application can be made in industry or used, in a technical sense.

5. Clarity

5.1 The independent claims state that polymer A is formed by reacting the compounds aa), ab) and optionally ac). However, such a formulation does not adequately define polymer A since, in principle, any chemical reaction can be used to produce A. Thus polymer A itself can have any chemical structure; for example, claim 1 would allow a phenol or a quinone to be reacted with one of the polyamines listed in a pyrolysis reaction, which would produce compounds that certainly would not be suitable for treating metal surfaces as per the application.

5.2 Most parts of the description describe polymer A merely as being "composed" of compounds aa), ab) and optionally ac), which can also be interpreted to mean that the polymer is not necessarily produced by reacting these components but contains aa), ab) and ac) as structural elements. However, this is not in keeping with the teaching of the present application; for example, polymer A no longer contains any aldehyde group, since it is converted into a methylene group in a Mannich reaction.

Therefore the corresponding parts of the description are not sufficiently in line with the claims.

5.3 Claims 1 and 4 contain the additional phrase whereby the composition is also suitable "for depositing metals or metal alloys onto synthetic material surfaces". However, deposition onto synthetic material surfaces is not an aspect of the present invention and, as the applicant has already been informed, is considered a separate invention.

Although these claims define a substance mixture which exists independently of the intended purpose, the additional phrase whereby said mixture is also suitable "for depositing metals or metal alloys onto synthetic material surfaces" is considered an attempt to include other aspects of the method and use which do not belong to this invention and have already been separated out in the discussion on unity of invention.

Consequently, the insertion of the above phrase renders the invention as a whole unclear.

5.4 The majority of the claims claim a certain combination of technical elements to which one or more further technical elements can be added "optionally". It should be noted that using the term "optionally" just once amounts to incorporating a dependent claim in the claim in question. The claims thus become confused and hence unclear if "optionally" can be added to more than one further technical element to produce a specific combination of technical elements, or if elements are linked by "and/or" (as in claims 2 and 3). Thus claim 1, for example, can already be interpreted as four independent claims. In this context, it is impossible to establish the subject matter claimed in claims 2 to 5, 8 and 9, which ultimately amount to 16 dependent claims. The applicant is referred to PCT Gazette, Section IV, paragraph III-3.7 (page 17).

5.5 Furthermore, component F is introduced into claim 3 as a further corrosion inhibitor. In the preceding claims, however, no component is identified as a corrosion inhibitor. Pursuant to PCT Article 6 and PCT Rule 6.2(a) (see also PCT Gazette, Section IV, paragraph III-4.10), the claims must be clear *per se*, without recourse to the description or drawings.

5.6 Claim 12 cannot be dependent on claims 1 to 5 since claim 12 covers more elements than claim 1.

5.7 Claims 8 and 9 mention a washing step with water three times. Since the claimed method only comprises steps a) to g), no sequence is given. Two of these washing steps in the list are therefore redundant.

5.8 Claims 7 and 10 are identical.

5.9 Formula IV on page 9 contains a phenolic structural unit not a quinoid unit, as mentioned in the first line on that page.

5.10 Page 32, line 4, should obviously read "polymers A", not "polymers C".

Defects:

The present application does not meet the requirements of PCT Rule 5.1(a)(ii), since D1, D2, D4, D5 and D8 are not mentioned in the introductory part of the present application, which also fails to cite the relevant prior art contained therein.

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claims as enclosed to IPER

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What is claimed is:

1. A composition for the treatment of metal surfaces or for the deposition of metal or
15 metal alloys on plastics surfaces, comprising

b) water or another solvent suitable for dissolving, dispersing, suspending or
emulsifying the polymer (component A), as component B;

20 c) if desired, surface-active compounds, dispersants, suspension media and/or
emulsifiers as component C

wherein the composition comprises

25 a) at least one polymer as component A, composed by reaction of
aa) at least one amino-containing polymer as component Aa;
ab) at least one aromatic compound as component Ab, being a phenol or quinone
or containing a phenolic or quinonoid structural unit;
ac) if desired, an aldehyde as component Ac.

30 2. A composition as claimed in claim 1, for the treatment of metal surfaces comprising
further to components A, B and, where appropriate, C

d) at least one salt, acid or base based on transition metal cations, transition metal
oxo anions, fluorometallates or lanthanoids as component D,
and/or

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e) at least one acid selected from the group consisting of phosphoric acid, sulfuric acid, sulfonic acids, nitric acid, hydrofluoric acid, and hydrochloric acid, as component E.

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3. Composition as claimed in claim 2, comprising

f) at least one further corrosion inhibitor as component F,
and/or

g) compounds of Ce, Ni, Co, V, Fe, Zn, Zr, Ca, Mn, Mo, W, Cr and/or Bi as component G,
and/or

h) further auxiliaries and additives as component H.

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4. A composition for the treatment of metal surfaces or for the deposition of metal or metal alloys on plastics surfaces as claimed in claim 1, comprising further to components A, B and, where appropriate, C:

i) at least one metal oxide and/or metal salt as component I,

j) where appropriate, at least one complexing agent as component J.

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5. Composition as claimed in claim 4, comprising

k) where appropriate, at least one acid or an alkali metal salt or alkaline earth metal salt of the corresponding acid, as component K, and

l) where appropriate, further additions as component L.

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6. A process for the treatment of a metal surface, which comprises contacting the metal surface with a polymer (component A) composed by reaction of

aa) at least one amino-containing polymer as component Aa,

ab) at least one aromatic compound as component Ab, being a phenol or quinone or containing a phenolic or quinonoid structural unit, and

ac) if desired, an aldehyde as component Ac.

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ART 34 AND

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7. A process as claimed in claim 6, wherein the metal surface is contacted with a composition as claimed in either of claims 1 to 3.
- 10 8. A process as claimed in claim 7, comprising the steps of:
 - a) where appropriate, cleaning the metal surface to remove oils, fats, and dirt,
 - b) where appropriate, washing with water,
 - c) where appropriate, pickling to remove rust or other oxides, in the presence or
 - 15 absence of the polymer (component A) ~~as claimed in claim 1~~,
 - d) where appropriate, washing with water,
 - e) treatment of the metal surface in the presence of the polymer (component A) ~~as~~
~~claimed in claim 1~~.
- 20 9. A process as claimed in claim 8, additionally comprising the steps of:
 - f) where appropriate, washing with water,
 - g) where appropriate, aftertreatment, in the presence or absence of the polymer
 - 50 (component A) ~~as claimed in claim 1~~.
- 25 10. A process as claimed in claim 6, wherein the metal surface is contacted with a composition as claimed in claim 1, 2 or 3.
- cancel 11. The use of polymers composed by reaction of
 - aa) at least one amino-containing polymer as component Aa,
 - 30 ab) at least one aromatic compound as component Ab, being a phenol or quinone or containing a phenolic or quinonoid structural unit, and
 - ac) if desired, an aldehyde as component Ac

for the treatment of metal surfaces.

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claim 1

12. A composition as claimed in ~~any of claims 1 to 5~~, wherein the amino-containing polymer is selected from the group consisting of polyethyleneimine, polyvinylamine, poly(vinylformamid-co-vinylamine), polylysine, polyaminostyrene, amino-containing derivatives of polycarboxylates, reaction products of polyamines with carboxylic acids and/or sulfonic acids, and carboxymethylation products of polyamines.